UCRL-CONF-155633

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October 22, 2003

Nuclear and Space Radiation Effects Conference, Monterey, California, July 21-25, 2003

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Abstract

Positron annihilation spectroscopy was used to study microstructural changes in low-k interlevel dielectrics under emulated electron irradiation of up to 1 Mrad(Si) dose, and the impact of the degradation of materials properties on device performance.

I. Introduction

To continue improving the capabilities and performance of high-end semiconductor device, manufacturers began using low dielectric constant (low-k; k < 3) materials as interlevel dielectrics (ILDs). This lowers the signal propagation delay, which limits device speed, minimizes cross-talk between neighboring wires, and lowers power consumption. Such low-k materials with no prior use in the industry have only been characterized for use in benign environments, characteristic for the typical end user. Since the space electronics market does not represent a significant part of the business interest of the semiconductor industry, the burden of device characterization, selection and flight qualification falls on NASA and military institutions. The necessity for such investigations is further enhanced by the growing trend of using commercial off-the-shelf (COTS) devices, many of which will inevitably use low-k ILDs in advanced products.

In this work, we examine changes occurring in the microstructure of methyl-silsesquioxane (MSSQ) – a prospective spin-on low-k ILD candidate – induced by irradiation by high-energy electrons, emulating space radiation environments. We characterized (1) the optical properties of blanket low-k films by using an refractometer and a spectroscopic ellipsometer, (2) dielectric properties using mercury probe, and (3) local electron bonding configuration, using positron annihilation spectroscopy (PAS).

In PAS, positrons, the antiparticles of the electrons, are used to probe the local electronic structure of materials in terms of local electron density and electron momentum distribution [1]. In insulating materials, positrons can form a bound state with an electron, known as positronium (Ps). Ps is a hydrogen-like atom, which is formed similarly in a singlet (para-Ps) and triplet states (ortho-Ps, o-Ps for short). o-Ps has been established as a probe for mesoporous materials [2,3], yielding pore size distribution, density, pore connectivity, and open porosity fraction. Radiation-induced degradation of low-k films has recently been examined by PAS [4].

II. Experimental

The samples used in this study were porous methyl-silsesquioxane (MSSQ) films made by IBM, using a sacrificial porogen approach. MSSQ resin was mixed in a solution with a volatile polymer (porogen) with various weight fractions. Si wafers were spin-coated with the solutions and cured to vitrify the MSSQ and subsequently to decompose the porogen, which leaves behind pores embedded in the MSSQ matrix. The resulting microstructure is determined by the MSSQ-porogen system, many varieties of which have been studied in detail [5]. A sample description is given in *Table I*. The refractive indices (RI) and film thicknesses of the samples were measured at the time of production using a refractometer. The optical properties of the films were re-measured before irradiation, using a spectroscopic ellipsometer. A comparison, shown in *Table I* ("r" – refractometer; "e" – ellipsometer), indicates that no significant changes were detected.

Radiation effects from high-energy electrons were emulated by using the Compton electrons of a ^{60}Co gamma source. This source is accepted as a standard in the space radiation community for characterizing total dose effects in microelectronic devices. Four sample sets of all porosity values were prepared. One of them was kept as a control set, whereas the others were irradiated to cumulative electron doses of 10 krad(Si), 100 krad(Si), and 1 Mrad(Si) using high dose rates. Past evidence [4] and the present results describe characteristics, which are stable on a month time scale and are thereby considered as permanent. Hence, the dose rate is irrelevant for this work.

Table I Sample designation and description:

- MSSQxx, where xx stands for weight fraction of porogen in the MSSQ-porogen system (*f*)
- resultant porosity (ϕ), calculated from refractometry and ellipsometry data
- dielectric constant (*k*), measured with a mercury probe
- average film density, caculated from refractometry and ellipsometry data
- film thickness and refractive index (*RI*) at 632.8 nm wavelength measured at the time of production using a refractometer (r), and before irradiation, using an ellipsometer (e).

Designation	f (wt.%)	ϕ (%)	k	ρ (g/cm^3)	*Thickness* (nm)		*RI* @ 632.8 nm	
					(r)	(e)	(r)	(e)
MSSQ00	0	0	2.78	1.35	667	662	1.367	1.372
MSSQ15	15	12.7	2.51	1.20	702	707	1.291	1.292
MSSQ35	35	29.7	2.03	0.98	728	719	1.196	1.199
MSSQ50	50	42.4	1.78	0.82	748	715	1.124	1.155
MSSQ60	60	50.9	1.82	0.70	681	697	1.123	1.123

Ps was used to probe the electronic structure of the low-k samples, and to detect radiation-induced changes. Detailed description of the Ps formation and interactions in low-k materials can be found elsewhere [3]. Relevant to this work is the annihilation channel of a Ps atom. Predominantly, the annihilation of the positron of a Ps atom with its paired electron (free annihilation) is accompanied with the emission of predominantly 3 photons (3γ), whereas the annihilation with a "foreign electron" (called pick-off annihilation) undergoes via 2 photons (2γ). The strong interaction of Ps with bonds, severed by ionizing radiation, virtually eliminates the 3γ annihilation [4], thereby changing the overall ratio of the 2γ and 3γ Ps annihilation channels. Hence, the attenuation of the 3γ Ps signal is identified with the increase of the density of unsaturated bonds.

A variable energy positron beam was used to depth-profile the 3γ-to-2γ annihilation ratio [1] in the low-k films. The scale was calibrated to measure Ps fraction using the results of Ref. [3], thus achieving better than 1% accuracy for relative changes with respect to the control set of unirradiated samples.

III. Results and discussion

Fig. 1 shows the depth profiles of the 3γ-Ps signal in the control set and the set irradiated to 100 krad(Si) dose. A decrease in the Ps fraction is observed in all samples. The relative change was estimated as $(x_0-x)/x_0$, where x_0 and x denote the Ps fraction before and after irradiation, respectively. All films show relative signal suppression between 6% and 8%, which indicates that the changes incurred by the electron dose are nearly independent on porosity of the film.

The dose dependence of the Ps signal is seen in Fig. 2, which shows the 3γ Ps profiles of MSSQ15 films: the control sample, and 10 krad(Si), 100 krad(Si), and 1 Mrad(Si) electron dose. The decrease of the 3γ Ps annihilation is evident. Using these data, we estimated a Ps loss rate between 13% and 17% per Mrad. Further experiments are planned to better this estimate by using samples irradiated to doses in the 0.1–1 Mrad(Si) range, since the dose dependence appears to be linear.

After the measurements, shown in Figure 2, the four MSSQ15 samples were annealed for 85 minutes on a hot plate at 150 ºC in air ambient (MSSQ does not react with oxygen). Water is known to corrode MSSQ when absorbed over a lengthy periods of time; however, moisture absorption from the air is virtually impossible at these temperatures. Figure 3 shows the results from the re-measured samples after anneal. With the exception of the 100 krad(Si) irradiated samples, which can be due to surface contamination, the annealed samples appear indistinguishable from each other. While the changes induced by the electron irradiation are successfully annealed, the Ps signal is still lower than that of the control sample (line), suggesting small irreversible changes.

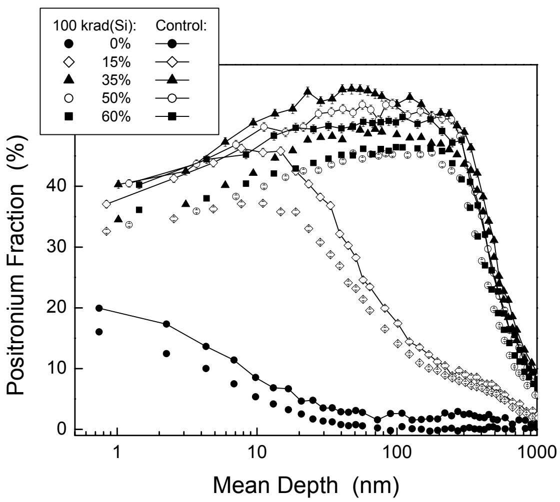

Figure 1. Depth profiles of the 3γ Ps signal in low-k films with different porosity (0-50%). The data for two set are shown: control samples (line+symbol) and after irradiation (^{60}Co) to a dose of 100 krad(Si). All irradiated samples show 6-8% suppressed Ps signal with respect to the control samples.

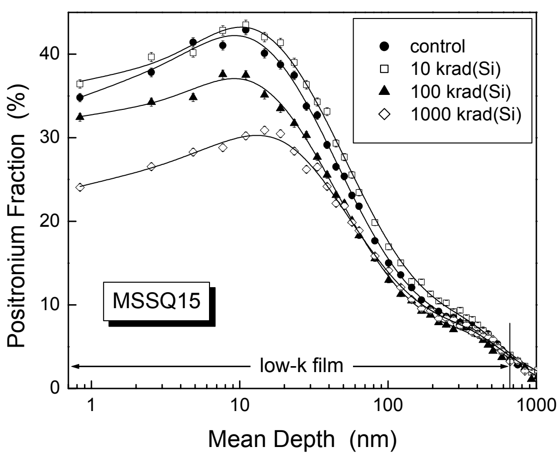

Figure 2. Depth profiles of the 3γ Ps signal in the 15% porous low-k films, before and after high-energy electron irradiation to cumulative doses of up to 1 Mrad(Si).

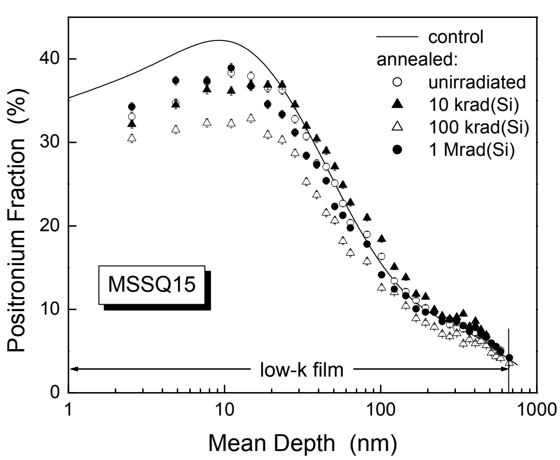

Figure 3. The 3γ Ps profiles of irradiated and unirradiated MSSQ15 samples after 150ºC hot-plate anneal in air ambient (symbols). The data for the control sample (no irradiation, no annealing) are given by the solid line.

The data shown in Fig. 1 indicate that the radiation damage to the MSSQ films is not porosity dependent. This evidence supports our interpretation of the suppressed 3γ Ps annihilation by the presence of unsaturated electron bonds, which were severed by the ionizing radiation. Since the degree of polymerization is similar for all cured MSSQ films regardless of porosity, the bond density is a characteristic of the bulk MSSQ matrix. This infers that the decrease observed by a probe (such as Ps), whose signal scales proportionally to the broken bond density, should be independent on porosity. This is confirmed by the relative 6-8% change, deduced from Fig. 1. Considerations can be made to extract a quantitative relationship between the relative suppression of the 3γ Ps and the density of broken bonds. Further work, which will result in a more accurate determination of the dependence of the 3γ Ps signal on radiation dose is warranted.

Reasonable concerns of using low-k ILDs in space radiation environments can be raised because of their polymeric nature. These are materials, whose structure can change on a microscopic level (e.g, degree of polymerization). This, in turn, can affect their mechanical, thermal, and electrical properties. Similarly, moisture absorption can change dramatically. One can envision plausible failure scenarios, such as:

- *Changes in signal propagation (RC) delay, which can offset timing synchronization*

The reconstruction of broken bonds tends to create different networks, which can increase the dielectric constant.

- *Deterioration of elastic properties, which can lead to loss of mechanical integrity*

Radiation exposure increases the degree of polymerization, which makes the low-k materials more brittle. Concerns about mechanical integrity have already been raised because of the use of 10-100 times weaker than SiO_2 non-porous materials, and porosity lowers further the mechanical strength (~10 times at 50%). Further deterioration of fracture toughness caused by ionizing radiation can be detrimental.

Measurements of dielectric constant and refractive index by conventional electrical and optical techniques yielded negligible changes in the properties of the studied films. Our results imply that MSSQ is relatively resistant to changes induced by space-like radiation environments, probably because it has SiO_2-like structure as opposed to some organic low-k ILD polymers. Nevertheless, radiation effects are easily detected by PAS, and further studies are needed to determine the consequences of microstructural changes on relevant properties. Encouraging is the fact that annealing can partially reverse the damage.

This work was performed under the U.S. DOE by University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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